THERMAL CONDUCTIVITY OF GAS MIXTURES AT HIGH PRESSURE

BY

WILLIAM ARTHUR JUNK, JR.

B.S., Pennsylvania State College, 1948
M.S., University of Illinois, 1950

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Introduction

Comings and Nathan (2) have developed a general correlation for the thermal conductivity of gases by using viscosity data for gases under pressure and P-V-T data to evaluate the constants in Enskog's equations (3). These were then used to calculate the thermal conductivity ratio, k/k_1, where k_1 is the thermal conductivity at atmospheric pressure. These values were employed in the preparation of a chart showing the variation of the thermal conductivity ratio with reduced pressure at constant reduced temperature.

Lenoir (6) measured the thermal conductivity of seven gases at pressures up to 200 atmospheres. When he compared his values with the Comings and Nathan correlation, he found that they agreed fairly will in general, but that there were discrepancies in the critical region. A better correlation was obtained by assuming that these gases obeyed the theorem of corresponding states and plotting the experimental thermal conductivity ratio versus reduced pressure.

It is the purpose of this investigation to measure the thermal conductivity of several binary gas mixtures and to extend the correlation to include these mixtures. Four mixtures of nitrogen and ethylene and two mixtures of carbon dioxide and ethylene have been measured at a temperature of 107.7°F and at pressures up to 200 atmospheres.

A redetermination of the thermal conductivity of ethane was included in this work. In a previous investigation (4), it was observed that in the high pressure region, the experimental values for ethane were 40% lower than those predicted by the theorem of corresponding states. There was also an abnormally sharp rise in the thermal conductivity with pressure followed by a rapid decrease in the region near the critical.

Theory

The theorem of corresponding states as applied to thermal conductivity assumes that all gases have the same thermal conductivity ratio when at the same reduced temperature and reduced pressure. This theorem may be extended to include binary mixtures by employing the pseudocritical method proposed by Kay (5). In this method the pseudocritical temperature and pseudocritical pressure are taken as the sum of the critical temperatures or critical pressures of the constituents of the mixture multiplied by their respective mol fractions. These pseudocritical constants are then used in place of the actual critical constants in the correlation for pure gases.

Experimental Procedure

The apparatus employed consisted of two very thin concentric gas filled annuli which were enclosed between steel cylinders. A radial temperature gradient was produced across these annuli by circulating hot water around the outside and cooler water through the center. The temperature difference between positions in the steel walls on each side of the gas layers was measured by thermocouples. The sample gas was placed in the inner annulus while the outer layer was filled with methane at one atmosphere to provide a constant thermal resistance which was used to indicate the relative rate of flow of heat. Thermal conductivities were measured indirectly, the apparatus being calibrated by filling the test layer with four different gases at one atmosphere. The conductivities of these gases were taken from the literature.

Results

It was found that the data for the nitrogen-ethylene mixtures could be correlated by means of the theorem of corresponding states and Kay's pseudocritical method with an average deviation of about 5%. This method was somewhat less satisfactory for the carbon dioxide-ethylene mixtures, however, the average deviation being 36% in this case. It

was found that for the latter system, the conductivities of the mixtures were generally lower than that of either of the pure components at the same pressure. Table I compares the smoothed experimental values with those calculated from the theorem of corresponding states.

The data for the ethane agreed with the previous measurements within the limits of experimental accuracy. It is thought that the irregular increase in conductivity near the critical density may be due to the tendency of the molecules to form clusters in this region. The low conductivity in the high pressure range may be explained by assuming that pressure acts to inhibit the transfer of energy by the internal degrees of freedom of the molecules.

TABLE I

Comparison of the Experimental Thermal Conductivities with Those Calculated from the Law of Corresponding States

Composition % C_2H_4	Pressure Atm.	k_{exp} BTU/Hr.Ft.°F	k_{calc} BTU/Hr.Ft.°F	% dev.
NITROGEN-ETHYLENE MIXTURES				
79.2	200	0.0377	0.0422	11.6
	100	0.0238	0.0248	3.9
	1.0	0.0133		
67.5	200	0.0337	0.0347	6.9
	100	0.0214	0.0222	3.2
	1.0	0.0136		
38.8	200	0.0251	0.0269	7.4
	100	0.0192	0.0195	1.5
	1.0	0.0143		
20.0	200	0.0228	0.0246	8.0
	100	0.0182	0.0193	5.8
	1.0	0.0152		
CARBON DIOXIDE-ETHYLENE MIXTURES				
55.5	200	0.0461	0.0665	45.3
	100	0.0323	0.0457	41.1
	1.0	0.0120		
79.8	200	0.0477	0.0627	31.1
	100	0.0330	0.0412	25.5
	1.0	0.0125		

The experimental thermal conductivity data for these six mixtures and for ethane are tabulated in the thesis.

Conclusions

1. Thermal conductivities of binary mixtures may be predicted by the theorem of corresponding states by using Kay's pseudocritical method. This method becomes less reliable, however, if one of the components is near its critical temperature.
2. Complex molecules which have considerable energy associated with their internal degrees of freedom may deviate considerably from the theorem of corresponding states in the high pressure region.
3. Gases may show an abnormal increase in thermal conductivity near the critical point due to the tendency of the molecules to form clusters.

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VITA

The author was born on March 12, 1924 in Uniontown, Pennsylvania. Following his graduation from Uniontown High School in June, 1942, he entered the Pennsylvania State College in the curriculum of Chemical Engineering. In May, 1943, he enlisted in the Army of the United States and served in the Mediterranean and European Theaters of Operation. Upon his discharge in November, 1945, he resumed his studies at the Pennsylvania State College until his graduation in June, 1948 with the degree of Bachelor of Science. In September, 1948, he entered the Graduate College of the University of Illinois from which he received the degree of Master of Science in June, 1950. He held a Teaching Assistantship in the Division of Physical Chemistry from 1948 until 1950. He also held the Standard Oil Company (Indiana) Fellowship from September, 1950 until June, 1951 and a University of Illinois Fellowship from September, 1951 until February, 1952.